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RESEARCH MEMORANDUM

AVERAGE BOND ENERGIES BETWEEN BORON AND ELEMENTS OF THE FOURTH, FIFTH, SIXTH, AND SEVENTH GROUPS OF THE PERIODIC TABLE

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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SUMMARY

The average bond energies $\overline{D}_{gm}(B-Z)$ for boron-containing molecules have been calculated by the Pauling geometric-mean equation. These calculated bond energies are compared with the average bond energies $\overline{D}_{exp}(B-Z)$ obtained from experimental data. The higher values of $\overline{D}_{exp}(B-Z)$ in comparison with $\overline{D}_{gm}(B-Z)$ when Z is an element in the fifth, sixth, or seventh periodic group may be attributed to resonance stabilization or double-bond character.

INTRODUCTION

Only recently have accurate thermochemical data on boron-containing molecules become available. These data (refs. 1 to 7) permit the calculation of a number of experimental average bond energies $\overline{D}_{exp}(B-Z)$, usually from reactions of the type

$$BZ_3(g) \rightarrow B(g) + 3Z(g)$$

In this paper the electronegativity of boron and the boron-to-boron bond energy are calculated and used to compute the $\overline{D}_{gm}(B-Z)$ bond energies from the Pauling electronegativity equation. The calculated values of $\overline{D}_{gm}(B-Z)$ are compared with the experimental values, and the differences between the values are interpreted in terms of partial double-bond character and resonance in BZ_3 compounds.

CALCULATIONS

The average bond energies are calculated from the equation (ref. 8)

$$\overline{D}_{gm}(B-Z) = \sqrt{D(B-B)D(Z-Z)} + 23.06(x_B - x_Z)^2 \qquad (1)$$

where $\sqrt{D(B-B)D(Z-Z)}$ is the geometric mean of the nonpolar bond energies and x_B and x_Z are the electronegativities of atoms B and Z (ref. 9). The geometric-mean rather than the arithmetic-mean equation (ref. 8) is used because the geometric-mean equation gives more satisfactory values of covalent bond energies when the atoms concerned are not alike. In any subsequent use of this equation or the expression D(Z-Z), Z will be replaced by the proper atomic symbols.

3878

The heats of formation of BH_3 and BR_3 ($R = CH_3$, C_2H_5, etc.), along with the new value of 141 kcal per mole for the heat of sublimation of boron, are used to calculate a $\overline{D}_{exp}$(B-H) of 93 kcal per mole and a $\overline{D}_{exp}$(B-C) of 87 kcal per mole.

By use of equation (1), two simultaneous equations can be solved for D(B-B) and the electronegativity of boron x_B. In one equation, $\overline{D}_{exp}$(B-H), D(H-H) (ref. 10), and x_H (ref. 11) are known; in the other equation $\overline{D}$(B-C), D(C-C) (ref. 10), and x_C (ref. 11) are known. Solving these equations gives D(B-B) of about 80 kcal per mole and x_B of 2.0. Using different data, Pauling (ref. 8) previously estimated an electronegativity of 2.0 for boron.

Another method of obtaining D(B-B) uses the dissociation reactions of BH_3, B_2H_6, B_5H_9, and $B_{10}H_{14}$ to B(g) and H(g) (ref. 12), along with the valence bond treatment recently proposed (ref. 13), to calculate a D(B-B) of about 85 kcal per mole.

To compute $\overline{D}_{gm}$(B-Z), values from reference 11 for the nonpolar bond energies and the electronegativities are used, except for D(N-N), D(S-S), x_N, x_S, and D(Ge-Ge). For D(N-N), the bond dissociation energy of 60 kcal per mole obtained from the homogeneous dissociation of N_2H_4 into NH_2 radicals (ref. 9) is used. Recalculation of the electronegativity differences for N-H, N-F, and N-C results in an x_N of 3.05 (fortuitously the same as x_N in ref. 11). For D(S-S), a value of 61 kcal per mole is obtained from

$$HS\text{-}SH(g) \rightarrow 2\ SH(g) \quad \text{and} \quad S_8(g) \rightarrow 8S(g)$$

using the values D(H-SH) of 90 kcal per mole, D(H-S) of 84 kcal per mole, $\Delta H_f^o(SH(g))$ of 32 kcal per mole, and $\Delta H_f^o(S(g))$ of 64 kcal per mole (ref. 14). Recalculation of the electronegativity differences of S-H, S-F, S-Cl, and S-Br results in an x_S of 2.75. A D(Ge-Ge) of 46 kcal per mole is used, based on $\Delta H_{subl.}(Ge(g))$ of 92 kcal per mole (ref. 15). The value of x_{Ge} given in reference 11 should not change appreciably (x_{Si} = 1.90; x_{Ge} = 1.90; and x_{Sn} = 1.90 (ref. 11)).

RESULTS

The calculated bond energies for bonds between boron and hydrogen and between boron and elements of the fourth, fifth, sixth, and seventh groups of the periodic table are listed in table I. Average bond energies obtained from various thermochemical studies are also listed in table I along with the molecule from which the thermochemical data were obtained.

DISCUSSION

The experimental values of $\bar{D}(B-Z)$, when Z is a fifth, sixth, or seventh group element in BZ_3 type compounds, are all higher than the calculated values. Since the calculated bond energies are for single bonds, this result is not surprising. When boron forms compounds with elements having unshared electron pairs and the boron has a six-electron valence shell (sp^2 hybridization of boron in BZ_3 compounds), the tendency is to fill up the valence shell by formation of structures of the type $Z_2B^- = Z^+$, often with several resonance forms possible (refs. 8 and 16). Therefore, B-Z bonds should have appreciable double-bond character and resonance stabilization, and should have higher bond energies than those calculated for single bonds. Thus, for B-F, B-Cl, B-Br, and B-I bonds, the strengthening (table I) amounts to about 17 kcal per mole per bond for B-F, about 10 kcal per mole per bond for B-Cl, and about 9 kcal per mole per bond for B-Br and B-I. Similarly, the B-O bond in $B(OC_2H_5)_3$ is about 15 kcal per mole stronger than calculated, while the B-O bond in $(\underline{n}\text{-}C_4H_9)_2BOH$ appears to be almost 30 kcal per mole stronger than the calculated value. Also, the B-N bonds in $B(N(CH_3)_2)_3$ and $B_3N_3H_3Cl_3$ (B-trichloroborazole) are 9 and 12 kcal per mole stronger than calculated, respectively. It is of interest to note the decreasing strengthening of the bond going down and to the left of F in the periodic table, that is, going from BF_3 to BI_3 and across to $B(N(CH_3)_2)_3$. The rather large difference between the bond strengthenings in $B(OC_2H_5)_3$ and $(\underline{n}\text{-}C_4H_9)_2BOH$ possibly indicates a very large double-bond character for $(\underline{n}\text{-}C_4H_9)_2BOH$ of the form $(\underline{n}\text{-}C_4H_9)_2B^- = OH^+$. These results are supported by the estimate that resonance stabilization in borate esters $B(OR)_3$ should exceed 17 kcal per mole based on a rough thermochemical determination (ref. 17).

Further support is provided by the estimate (from thermochemical data other than those used in this paper) that the single-bond B-F bond energy should be between 130 and 140 kcal per mole (ref. 18), which is in agreement with the 137 kcal per mole calculated in the present investigation.

CONCLUDING REMARKS

Experimental results indicate that the Pauling geometric-mean equation does not successfully predict the actual bond energies for compounds formed between boron and fifth, sixth, and seventh group elements of the form BZ_3, since they have some multiple-bond character. The Pauling equation in its usual form is set up to calculate single-bond energies. On the other hand, the comparison of the hypothetical single-bond energies with the actual energies provides a method of estimating the amount of bond strengthening resulting from multiple-bond character and resonance. The bond energies of boron-hydrogen and bonds involving boron and group-four elements (carbon, silicon, germanium, and tin) should be calculable from the Pauling equation, since these elements have no unshared electron pairs. If stable covalent bonds exist between boron and alkali metals, their bond energies may also be calculable as single-bond values.

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3878

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3878

TABLE I. - AVERAGE BOND ENERGIES $\overline{D}(B-Z)$

Bond	$\overline{D}_{gm}(B-Z)$, kcal/mole	$\overline{D}_{exp}(B-Z)$,[a] kcal/mole	Source	References
B-H	92	93±2	BH_3	5,6
B-C	[b]89	87±3	BR_3 (R = CH_3, C_2H_5, C_3H_7, C_4H_9)	6
B-N	95	104±5	$B(N(CH_3)_2)_3$	4
		107±5	$B_3N_3H_3Cl_3$	2
B-O	104	119±5	$B(OC_2H_5)_3$	1
		133±5	$(\underline{n}-C_4H_9)_2BOH$	3
B-F	137	154±5	BF_3	6
B-Si	64	-----	------------	
B-P	64	-----	------------	
B-S	83	-----	------------	
B-Cl	98.5	108.5±2	BCl_3	6
B-Ge	61	-----	------------	
B-As	55	-----	------------	
B-Se	65	-----	------------	
B-Br	81.5	90±2	BBr_3,	7
			$(\underline{n}-C_4H_9)_2B(Br)$	3
B-Sn	53	-----	------------	
B-Sb	52	-----	------------	
B-Te	54	-----	------------	
B-I	62	71±5	$(\underline{n}-C_4H_9)_2BI$	3

[a]Experimental thermochemical values recalculated using $\Delta H_f^o(B_2O_3(s))$ of 305.4 kcal/mole and $\Delta H_{subl.}(B(s))$ of 141 kcal/mole.

[b]Based on D(C-C) of 82 kcal/mole.